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RESEARCH MEMORANDUM

DETERMINATION OF AROMATICS AND OLEFINS
IN WIDE-BOILING PETROLEUM FRACTIONS

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DETERMINATION OF AROMATICS AND OLEFINS

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SUMMARY

A method is described for the determination of aromatics and olefins in petroleum fractions with wide-boiling ranges by a combination of sulfonation, chromatography, and specific dispersion. Chromatography is used to separate the sample into a pure nonaromatic, an intermediate, and a pure aromatic fraction. Total aromatics are found as the sum of the pure aromatic fraction and the volume of aromatics in the intermediate fraction as determined by specific dispersion. Sulfonation yields the percentage of olefins plus aromatics and the percentage of olefins is determined by difference. Less than 8 hours are required per analysis. The method has been checked on blends of pure hydrocarbons and has been found to yield inaccuracies of less than 1 percent in the determination of olefins and aromatics.

INTRODUCTION

In order to understand more fully the effect of fuel variables in aircraft propulsion systems, it is often necessary to determine the concentration of olefin and aromatic hydrocarbons in petroleum products that are used as fuels. The most recent turbojet fuel specification (AN-F-58a) calls for a wide-boiling fuel with 5 to 7 pounds per square inch Reid vapor pressure and a 600° F maximum end point. Aromatics up to 25 percent and olefins equivalent to a 30 bromine number are permitted.

A review of the available literature made at the NACA Lewis laboratory showed that the following general methods of analysis might be applied to fuels of the AN-F-58a type:

In the A.S.T.M. procedure D 875-46 T (reference 1) in which olefins and aromatics are absorbed by a mixture of sulfuric acid and phosphorus pentoxide, olefins are calculated from bromine number and aromatics are obtained by difference. The concentrations of paraffins and cycloparaffins can also be estimated from the older A.S.T.M. method

ES-45a (reference 2) using refractivity intercept and the density of the raffinate from the sulfonation. Although the accepted method of analysis under the AN-F-58a specifications is the A.S.T.M. method, occasionally inaccurate results will be obtained by the use of this procedure. The greatest weakness of this method appears to be in the calculation of the percentage of olefins from bromine number and the molecular weight, where the average molecular weight of the olefins should be used and not the molecular weight of the total sample. The molecular weight is estimated from the 50-percent boiling point of the total sample in the A.S.T.M. procedure, which often results in substantial errors in the calculation of the percentage of olefins. Errors in percentage of olefins are also reflected as equal errors of opposite sign in the determination of the percentage of aromatics by the A.S.T.M. procedure.

The A.S.T.M. silica-gel method D 936-47 T (reference 3) applies to fuels containing less than 1 percent olefins and therefore does not cover the AN-F-58a specifications.

Another general method relies on chromatography alone to split samples into paraffin and cycloparaffin, olefin, and aromatic fractions. Mair (reference 4) and Dinneen (reference 5) proposed this type of analytical separation. Both show its effectiveness on relatively simple blends and Dinneen also gives data on shale oil naphthas (reference 5). Although good separations are obtained on multicomponent blends of pure hydrocarbons, an olefin plateau is not obtained in the chromatographic fractionation of the complex fuels when small amounts (10 percent or less) of olefins are present. This method is therefore not universally applicable to fuels meeting the AN-F-58a specifications.

Grosse and Wackher (reference 6) developed a method for the determination of aromatic hydrocarbons in fuels based on the measurement of the specific dispersion of the sample. The relative uncertainty of the method on turbojet-type fuels lies in the inaccuracy of the olefin determination and in not knowing the specific dispersion of the aromatics present in the fuel.

Conrad (reference 7) developed a rapid method for the determination of aromatic compounds in fuels of the gasoline and kerosene range based on chromatography and ultraviolet stimulated fluorescence. Limited experience with this method has shown it to be less reliable as the complexity of the aromatics and the olefinic content increase, as is the case with AN-F-58a fuels. Also, provision is not made to obtain fractions of saturates or aromatics on which further studies can be made.

Although the procedure of Kurtz and others (reference 8) is recommended for the analysis of samples having end points no higher than 437° F, it is probable that the method could be modified to include the 600° F end-point fuels. The method requires a fractional distillation and the determination of the volume percentage absorbed by sulfuric acid - phosphorus pentoxide, bromine number, specific dispersion, and the percentage of olefins by the nitrogen-tetroxide method on each of the fractions. Apart from the uncertainty as to whether the method could be extended to the higher end-point fuels, the principal objection to this procedure is the necessity of running a fractional distillation, which requires about 24 hours, and the relatively large number of determinations that must be made on the many distillation fractions.

A method that has been in use at the Lewis laboratory for over a year and has appeared quite satisfactory uses chromatography to separate a nonaromatic fraction, an intermediate fraction, and a pure aromatic fraction. In order to make the separation more apparent, Parasheen was used as recommended by Conrad (reference 7). The percentage of aromatics in the intermediate fraction is then determined by the specific-dispersion method of Grosse and Wackher (reference 6). Although high precision cannot be obtained in the analysis of wide-boiling fuels by this method, the inaccuracies are confined to only a small part (about 10 percent) of the whole fuel and the error in the analysis of the total fuel is only about 10 percent of what it might have been had the aromatics in the total sample been determined by the same method. The percentage of olefins is obtained by the difference between the total olefins and aromatics from the A.S.T.M. sulfonation (D 875-46 T) procedure and the aromatics as determined by the proposed procedure. An aromatic fraction is also obtained, which can be further characterized, if desired, and paraffins and cycloparaffins can be determined on the sulfonation raffinate (reference 2).

This method for determining aromatics and olefins in jet-type fuels is described herein and supporting data on multicomponent blends are given. Some results on typical turbojet-type fuels are also included.

APPARATUS AND MATERIALS

The apparatus and the materials used in this determination are as follows:

1. A pyrex glass adsorption column as described in A.S.T.M. method D 936-47 T (reference 3) without the stopcock and ground-glass joint at the bottom.

2. Activated silica gel 28-200 mesh. Finer than 200-mesh gel may also be used with similar results, but the analysis will require a greater length of time. The Davison Chemical Corporation, Baltimore, Md.

3. Graduated mixing cylinders; 100-, 25-, and 10-milliliter sizes

4. Sulfonation bottles, Kimble No. 15125

5. Refractometer capable of measuring $n_D - n_C$ values to 0.0002

6. Mercury arc ultraviolet lamp, such as model 16200, manufactured by Hanovia Chemical & Manufacturing Company, Newark, N. J.

7. Isopropyl alcohol, c.p. grade. If the sample is suspected of containing high-molecular-weight aromatics, Carbitol used as the eluent will desorb these aromatics more completely.

8. Acidified calcium chloride solution. (450 g/liter + 20 ml concentrated hydrochloric acid)

9. Parasheen. Enjay Company, Paraflow Sales Department, Chemical Products, 26 Broadway, New York 4, N. Y.

PROCEDURE

The column, thoroughly cleaned and dried, was filled with activated silica gel and packed following the A.S.T.M. method (reference 3). A 100-milliliter sample containing two drops of Parasheen was introduced into the reservoir and allowed to percolate into the gel. In order to insure the complete transfer of the sample, the flask was rinsed with 2 or 3 milliliters of eluent (isopropyl alcohol) and the rinse added to the reservoir immediately after all the first portion of the sample had been adsorbed on the silica gel. When the rinse was completely adsorbed, the reservoir was filled with eluent and an air pressure of 3 to 10 pounds per square inch applied to maintain the desired rate of descent (7 to 13 mm/min). Additional eluent was added when necessary so as to keep the gel covered. In the samples where the aromatic content was under 10 percent, 90 milliliters of the sample were taken and 10 milliliters of pure isopropyl benzene added.

When the sample was about to issue from the bottom of the column, a glass-stoppered 100-milliliter graduated mixing cylinder was placed under the column to receive the nonaromatic fraction. These receivers

were packed in ice to reduce evaporation losses of the volatile components. As the column was not equipped with a ground-glass joint to accommodate this type of receiver, a tight seal was maintained by allowing the weight of the column to rest directly on the receiver with a little glass wool serving as a gasket. This connection was not airtight and therefore provided the necessary vent while keeping evaporation losses small.

As the fractionation progressed, the leading edge of the aromatic portion was located by using ultraviolet light in a dark room (or in a suitable dark box). The Parasheen tracer allowed this edge to be followed quite easily. Although the edge was found to be quite sharp for samples having low olefin content (5 percent or less), it became less distinct as the olefin concentration increased.

When the break point approached the column tip to within 5 centimeters, the cylinder receiving the nonaromatic fraction was replaced by a 10-milliliter graduated cylinder. A 10-milliliter intermediate fraction was then taken, which contained a sample from either side of the break point. The receivers were again changed and the major aromatic fraction up to 2 centimeters of the alcohol-aromatic break point, which was always visible, was removed. A final 10-milliliter fraction, including the remaining aromatics mixed with alcohol, was collected in a sulfonation bottle and the alcohol removed by washing with acidified calcium-chloride solution until the volume of the aromatics remained constant (usually three washings). The washing was accomplished by adding calcium-chloride solution to the bottle so that the level of the liquid was in the graduated neck, shaking the mixture into an emulsified condition, and centrifuging until the mixture separated into two layers. The spent calcium-chloride solution was removed by inverting the bottle, carefully loosening the stopper, and permitting most of the water solution to drain, leaving the aromatics in the bottle. Recovery of the sample was found to be 98 percent or better. The losses were assumed to be low-boiling paraffins, which escaped by evaporation.

In order to calculate the volume percentage of aromatics present in the sample, it is necessary to determine the aromatics in the intermediate fraction because the initial fraction is pure nonaromatic and the subsequent cuts are pure aromatics. The method employed is based on the measurement of the specific dispersion of the cut on an ordinary Abbe refractometer. The weight percentage of aromatics in the cut is given by the equation of Grosse and Wackher (reference 6).

$$\text{Weight percentage of aromatics} = \frac{\delta_{\text{cut}} - (0.16 \times \text{bromine number}) - 99}{\delta_{\text{aromatics}} - 99}$$

where

$$\delta \quad \text{specific dispersion} = \frac{n_F - n_C}{d} \times 10^4$$

and where

n_F refractive index measured at the wavelength of the hydrogen F line and at 20° C

n_C refractive index measured at the wavelength of the hydrogen C line and at 20° C

d density at 20° C

Direct measurement of n_F and n_C cannot be made but the difference $n_F - n_C$ can be determined on the Abbé refractometer. The specific dispersion of the aromatics present in the cut can be obtained from figure 1 knowing the A.S.T.M. 50-percent boiling point of the original sample (reference 6). In cases where isopropyl benzene was added, the specific dispersion of the aromatics was taken as 172.0 (reference 9). The bromine number is found by using the A.S.T.M. method (reference 1). The volume percentage of aromatics in the intermediate fraction can be calculated using the equation

Volume percentage of aromatics =

$$\text{weight percentage of aromatics} \times \frac{d_{\text{cut}}}{d_{\text{aromatics}}}$$

The density of the aromatics, chosen as 0.870 gram per milliliter, represents an average of a series of typical single-ring aromatics present in fuels. The total volume percentage of aromatics in the sample is equal to the sum of the aromatics in the intermediate cut plus that in the aromatic fraction and wash.

In the cases where the sample contained less than 10 percent aromatics and 10 milliliters of isopropyl benzene were added, the volume percentage of aromatics was corrected by the equation

$$(\text{Volume percentage of aromatics} - 10) \frac{10}{9} =$$

volume percentage of aromatics in sample

As previously mentioned, the olefins plus aromatics are determined on the original sample by the standard A.S.T.M. sulfonation method (reference 1) and the olefins obtained by the difference between this value and that of the aromatics mentioned.

The entire analytical procedure requires less than 8 hours.

If it is desired, the following information can be obtained. The paraffins and cycloparaffins can be computed from the sulfonation raffinate (references 2 and 10). The naphthalenes can be determined from the major aromatic fraction and wash by the ultraviolet spectrophotometric method of Cleaves and Carver (reference 11) and the average number of rings per molecule by the method of Lipkin and Martin (reference 12).

DISCUSSION OF RESULTS

In order to prove the accuracy of the method, 10 blends of paraffins, cycloparaffins, olefins, and aromatics covering the range of AN-F-58a specifications were analyzed by this procedure. The stocks used for the blending were mixtures of pure hydrocarbons representing the following types: straight- and branched-chain paraffins; cycloparaffins; straight- and branched-chain olefins, and cycloolefins; and single- and double-ring aromatics. The boiling range was from 160° to 580° F. Table I shows the composition of the stocks that were used. The paraffin stock was found to contain less than 0.1 percent aromatics by the ultraviolet method of Cleaves (reference 13). A slow chromatographic fractionation through 200-mesh silica gel of a blend of 45.0 milliliters of aromatic stock and 5.0 milliliters of certified isooctane indicated that the aromatic stock contained less than 0.3 percent of nonaromatic components. Each of the olefins showed less than 0.1 percent aromatics by the ultraviolet method (reference 13) and each had a bromine number that was within 2 percent of the calculated value. The composition of the test blends is given in table II and it can be noted that samples contained from 0-to 20-percent olefins and 0-to 25-percent aromatics, representing the specification limits.

The results of the test-blend analysis are given in table III. The average absolute error for aromatics and olefins was ± 0.3 percent. In table IV the results of analysis of several jet-type fuels are listed. Fuel A is a refinery-supplied fuel, which meets AN-F-58a specifications. To this fuel was added 8 percent of No. 3 furnace oil to give B fuel and 8 percent of No. 3 furnace oil plus 13 percent of Hydroformate bottoms to give C fuel. The No. 3 furnace oil and the Hydroformate bottoms were analyzed by a slow percolation through

200-mesh silica gel. The furnace oil was found to contain 29.3-percent aromatics and the Hydroformate 97.3-percent aromatics. Both were free of olefins; therefore the aromatic determinations were believed to be good. Also listed in table IV are the percentages of aromatics and olefins found in these three fuels using the A.S.T.M. sulfonation and bromine-number technique. Although the sums of the aromatics and the olefins are substantially the same as those obtained by the proposed method, the olefins average 5.3 percent higher and the aromatics 5.1 percent lower. These differences are largely due to inaccuracies in the molecular weights estimated by the A.S.T.M. procedure. These molecular weights were estimated at from 134 to 155 for these fuels, whereas fractional distillation followed by bromination of the fractions showed that the true average molecular weights of the olefins were very close to 90.

The theoretical values given in table IV for fuels B and C are those calculated from the determined percentages of olefins and aromatics for fuel A and the analysis of heavy components that were added to form them. The agreement between the analyzed and the calculated values show the method to be consistent at least for fuels containing heavy components.

One of these fuels, fuel A, was also analyzed in another laboratory using fractional distillation prior to the determination of aromatics and olefins in each fraction. By this more time-consuming method, 18.2-percent aromatics and 9.0-percent olefins were found, which is in satisfactory agreement with the results given herein.

CONCLUDING REMARKS

In the method described herein some well-known analytical procedures were combined to yield a chromatographic procedure for the analysis of aromatics and olefins in wide-boiling petroleum fractions with the following advantages:

1. Accuracies of the order of 1 percent were obtained.
2. The analysis required less than 8 hours.
3. Only four fractions were taken, and of these, analytical data were required on but one to determine the aromatics in the fuel.

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TABLE I - COMPOSITION OF STOCKS

Paraffin cycloparaffin stock	Volume percent	Aromatic stock	Volume percent	Olefin stock	Volume percent
<u>n</u> -Heptane	12.5	Benzene	15.0	Octene-1	33.3
<u>n</u> -Decane	12.5	Toluene	15.0	Diisobutylene	33.3
Iso-octane	25.0	Xylenes	20.0	Cyclohexane	33.4
Cyclohexane	12.5	Methylnapthalenes (α , β)	25.0		
Methylcyclohexane	12.5	Tetralin	25.0		
Decalin	25.0				
	100.0		100.0		100.0

TABLE II - COMPOSITION OF TEST BLENDS

Blend	Paraffin- cycloparaffin (volume percent)	Olefin (volume percent)	Aromatic (volume percent)
1	75	0	25
2	70	5	25
3	65	10	25
4	55	20	25
5	70	20	10
6	75	20	5
7	80	20	0
8	100	0	0
9	90	5	5
10	80	10	10


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TABLE III - RESULTS OF THE BLEND ANALYSIS

Blend	Aromatics			Olefins		
	Volume percent		Percent error	Volume percent		Percent error
	True	Found		True	Found	
1	25.0	24.6	-0.4	0	0.2	0.2
2	25.0	25.0	0	5.0	4.6	- .4
3	25.0	24.7	- .3	10.0	10.0	0
4	25.0	25.4	.4	20.0	19.6	- .4
5	10.0	10.2	.2	20.0	20.2	.2
6	5.0	4.9	- .1	20.0	20.3	.3
7	0	.8	.8	20.0	19.6	- .4
8	0	0	0	0	0	0
9	5.0	5.2	.2	5.0	5.5	.5
10	10.0	10.3	.3	10.0	10.0	0
Average error			±0.3			±0.3

TABLE IV - RESULTS OF REFINERY FUEL ANALYSIS

Fuel	Aromatics (volume percent)			Olefins (volume percent)			A.S.T.M. procedure	
	Theoretical	Found	Error	Theoretical	Found	Error	Percent aromatics	Percent olefins
A	(18.2)	18.2	-----	(7.2)	7.2	-----	14.0	11.5
B	19.1	19.8	0.7	6.6	6.2	-0.4	14.5	11.5
C	29.4	30.3	.9	5.7	5.4	- .3	24.0	12.0


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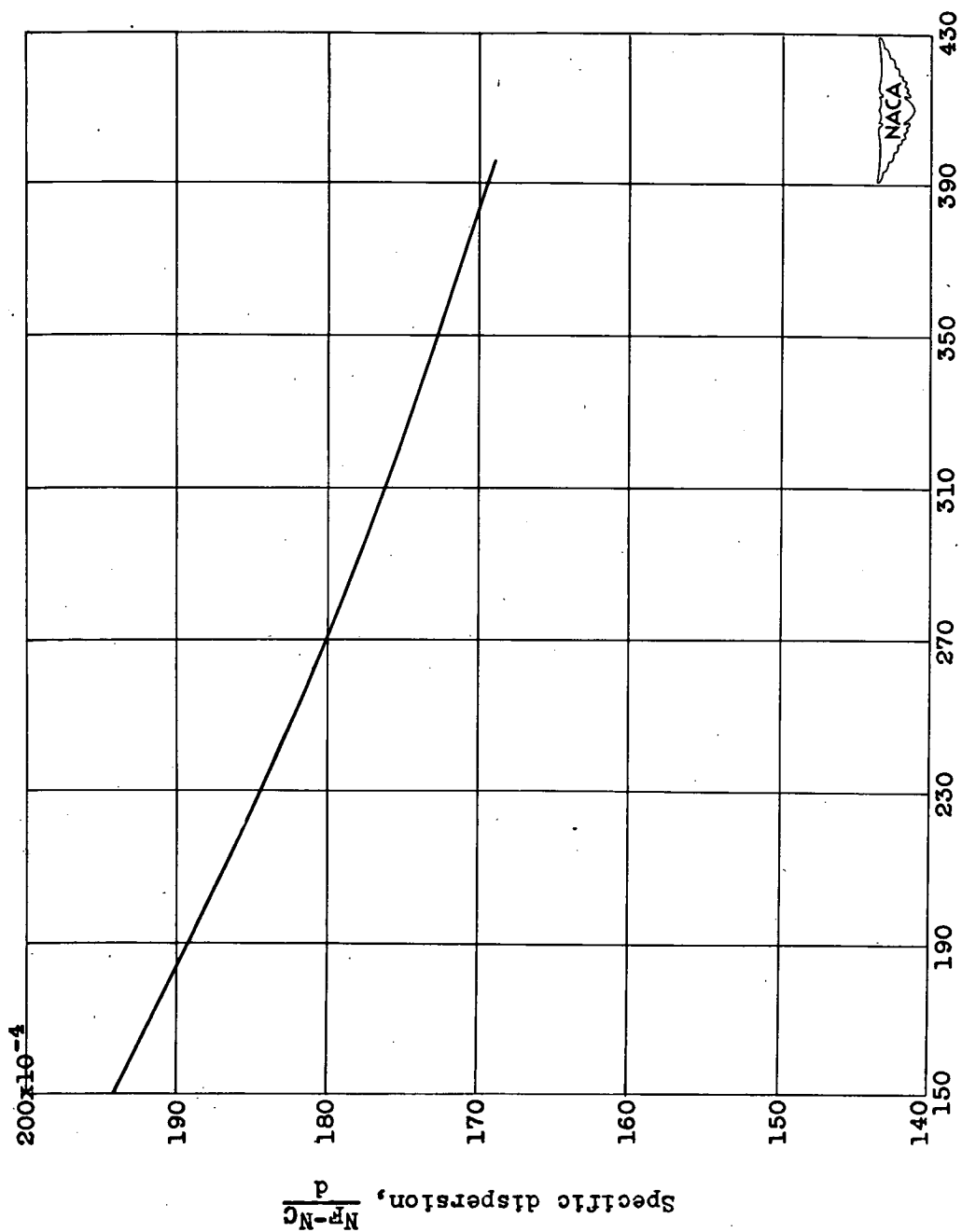


Figure 1. - Specific dispersion of alkylbenzenes as a function of the A.S.T.M. 50 percent boiling point.